End Of Project Report

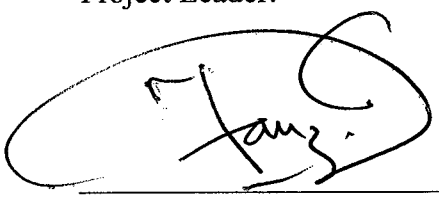
(NIPPON SHEET GLASS)

Period : 2005-2007

Project Title:

Synthesis of Ultrafine $Ba_{0.7}Sr_{0.3}TiO_3$ by Mechanically Activating Process

Project Leader:



Professor Dr. Ahmad Fauzi Mohd Noor

Tel: 05-5946174
Fax: 05-5991011

Profesor Dr. Ahmad Fauzi Mohd Noor
Pusat Pengajian Kejuruteraan Bahan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia,
14300 Nibong Tebal, Pulau Pinang.
Tel: 604-599 6174 Fax: 604-594 1011

Synthesis of Ultrafine $Ba_{0.7}Sr_{0.3}TiO_3$ by Mechanically Activating Process

1. Summary

The project 'Synthesis of Ultrafine $Ba_{0.7}Sr_{0.3}TiO_3$ by Mechanically Activating Process' was successfully completed early 2008. As reported in the technical report attached, the single phase BST was produced successfully at a relatively low temperature of 500°C, albeit the challenges encountered during the synthesis, one of which is the caking problem as well as melting of phase formed. The caking effect was due to the mechanical activation process, while the melting phase was a result of the low meting chemicals used.

Calcination at 500°C wasthe lowest that we can achieved in this study. It was found that during sintering, the next stage of product formation, the pellets prepared from 400°C calcined mixture cracked after sintering. This is due to insufficient decomposition at 400°C. Further significant decompotion took place during sintering which caused the pellet to crack.

The dielectric properties obtained in this studies were relatively low as compared to those derived from conventional solid state reaction route. The dielectric properties are most optimum in the grain size range of 2-5 μm, and subsequent declined if the grain size is smaller or bigger. Therefore ultrafine powder is expected to yield lower dielectric value, however it makes miniaturization possible which is crucial in electronic field. Furthermore, the decomposition of the remnant phase of $BaCO_3$ and $SrCO_3$ in the calcined powder contributed to the porous microstructure; hence degraded the dielectric properties.

2. Period of research conducted : 01/2005 to April 2008

The research was approved from Jan 2005 to Dec 2007. There was an extension of of a few months to the period of research. This was due to some complication in the beginning of the funding of the project. Although there was indication of the approval of the project, but the funding disbursed was only received middle of July 2005. Nevertheless, the project proceeded on after the fund was received.

3. Amount of fund :

Received:	RM37,643
Spend:	RM35,600
Balance:	RM2,043

4. Staff involvement

1 Final Year Project student
1 RA
1 PostDoc (supporting project)

5. Purchase of equipment: None

6. Publication : 1

Teoh Wah Tzu, K.Sato, Ahmad Fauzi M.N.; Properties of Ba0.7Sr0.3TiO3 Synthesised From Mechanically Activated Ba(OH)2.8H2O-Sr(OH)2.8H2O-TiO2 Solid System by Mortar Grining and planetary Milling, ITE Letters on Batteries, New Techniologies and Medicine, Vol.8, No. 3, (2007)

Conclusion

The project has been completed, with a successful outcome of synthesizing single phase BaSrTitanate. Upon sintering, it was found that a low dielectric constant material was produced, as compared to BST produced by solid state reaction. Nevertheless, the values achievd are still within the range of typical dielectric materials.Further work will be continued to produced BST with optimum dielectric properties.

Report prepared by

Professor Dr Ahmad Fauzi Mohd Noor.

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The project was successfully completed within the stipulated time. and managed to produce the intended product which was BaSrtitanate. A paper was published in a journal as well. Overall, the project has met the expected outcomes.

PROF. MADYA DR. AZIZAN AZIZ
Timbalan Dekan
(Pengajian Siswazah & Penyelidikan)
P.P.Kejuruteraan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia

A) Project Summary

$Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2 solid system had been investigated to produce $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) via solid state reaction by mechanical activation technique. Mechanical activation was performed to these solid systems by high energy planetary milling equipment.

In the preparation of single phase BST from starting materials of $Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2, remnant of carbonates are found in the solid system after calcination process; this was due to the localized inhomogeneous (caking effect) of the solid mixture by planetary milling. However, single phase BST was successfully derived from the sintered pellet of BST. The mechanically activated particle also achieved ultrafine size at the range of 200 nm. The powder is the undergone pelletization follow by sintering. Single phase BST was achieved for all the pellets sintered at 1250°C to 1450°C. The sintered pellets at 1450°C achieved the highest dielectric constant of about 7500. Properties comparison for this solid system with other studies is unable to perform due to lack of available literature in BST preparation from $Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2.

In general, this project had achieved its objective to produce single phase BST pellet by mechanical activation process with ultrafine particle size. The calcination process is carried out at temperature as low as 500°C to decompose most (but not all) of the hydrated H_2O. The dielectric properties obtained were within the expected range of value for ultrafine particles.

B) Project Background

In the technology-driven global market today, electronic devices ranging from common mobile phone, personal computers to sophisticated communication satellites have become part and parcel of our routine life. The performances of all these electronic devices inevitably rely on the functional materials that are used to assemble them. The ongoing drive for electronic devices miniaturization has force the necessity to reduce the size of these functional materials and also to discover better-performed materials. Therefore, the technological and economical significance of developing ultrafine functional materials without sacrificing too much of their electrical properties are enormous.

$Ba_{1-x}Sr_xTiO_3$ is an important ferroelectric-piezoelectric ceramic that has been widely used as dielectric materials in many electronic devices. The conventional method of synthesizing $Ba_{1-x}Sr_xTiO_3$ involves mixing $BaCO_3$, $SrCO_3$ & TiO_2 in stoichiometric ratio, followed by high temperature (>1000°C) solid state reaction. Although this method provides a simple & straight forward synthesis route but it is often leads to compositional inhomogeneous and particle coarsening. Several chemistry based method such as sol-gel, hydrothermal and co-precipitation which are able to produce homogeneous and ultrafine $Ba_{1-x}Sr_xTiO_3$ with certain heat treatment not exceeding 800^0C. However, these methods are often associated with the disadvantages such as very high manufacturing cost, low production yield and bringing ecological problems, which make them unsuitable for industrial scale production. Furthermore, most of them have yet to demonstrate any significant advantages over the conventional method.

Mechanical activation technique is derived from mechanical alloying method which develops for the production of composite powder, inter-metallic compound and amorphous metallic powder. It was later employed to synthesize various magnetic and powder by mechanically activated the starting materials through high energy milling. Mechanical activation technique has been successfully devised by researchers to synthesized single phase electronic ceramics powder. Although it is known that the technique works and so is useful, but it is not clearly understood than those thermally activated process. A number of research has been devoted to mechanical activation technique in recent years, there are still a number of problem to be address and eventually solved.

The intrinsic advantage of mechanical activation method lies in its ability to effect a solid state reaction through mechanical treatment, instead of by calcining at a high enough temperature, easily exceeding 1000°C by conventional method. It can also leads to an improvement in the reactivity of the starting materials and therefore the desired ceramic phase is formed at a lower calcination temperature. Mechanical activation is able to change the thermodynamic potentials of reagents and diminish the temperatures of the chemical reaction. Mechanical activation which is a energy-intensive homogenizing grinding process, helps to intensify transport of the reactants by intimate mixing of solid substances not only at the physical but also on a chemical level.

The relatively ease of producing mechanical activation-derived powder in large quantities compared to other nonconventional synthesis technique will be the key driving forces in propelling this process. Therefore, this technique shall be evaluated as an alternative synthesis route or a value added step in $Ba_{1-x}Sr_xTiO_3$ powder preparation.

C) Project Objectives

- Lowering the synthesis temperature of $Ba_{0.7}Sr_{0.3}TiO_3$ by mechanically activating mixtures of $Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2.
- Improved physical properties and dielectric properties of the $Ba_{0.7}Sr_{0.3}TiO_3$ produced

D) Project Research Approach

The processing of BST from $Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2 is shown in figure 1.

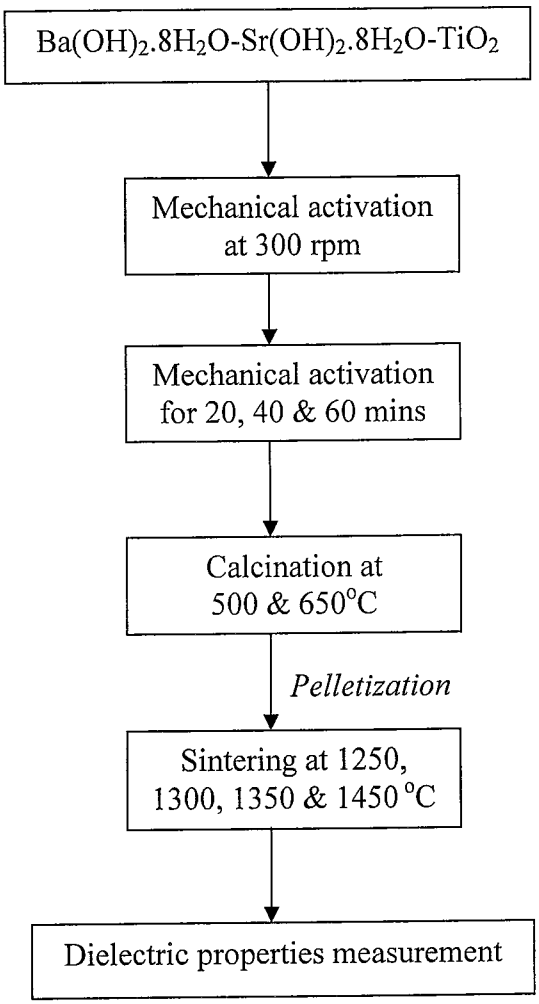


Figure 1: Processing flow of BST derived from $Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2

E) Project Result & Discussion

The dielectric performance of BST

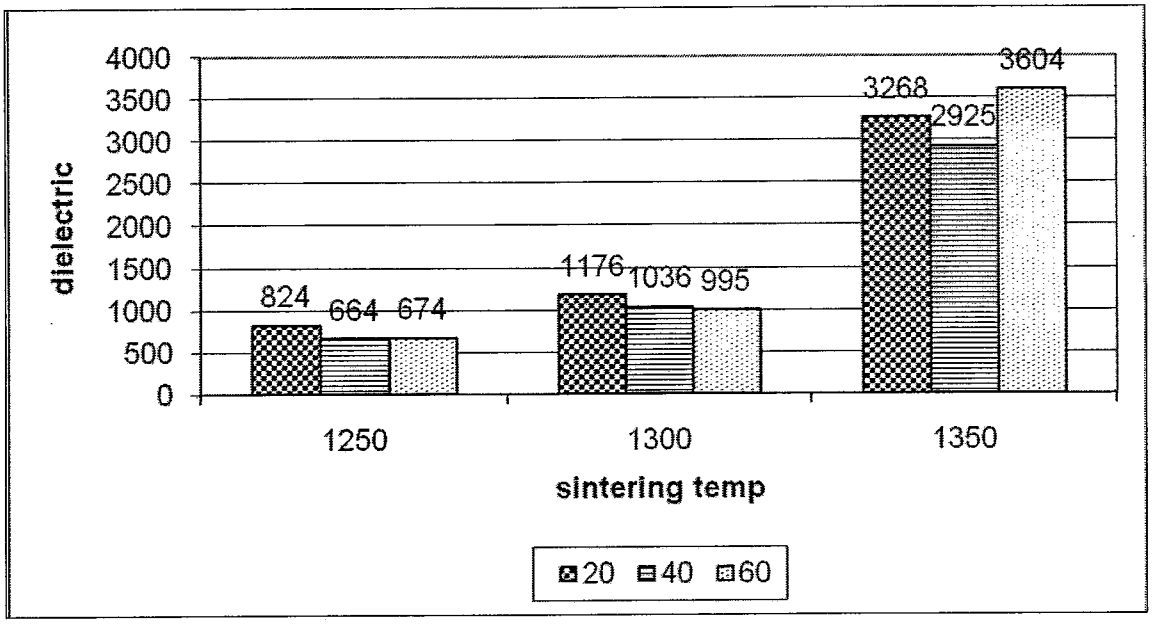


Figure 2: Dielectric constant value from samples derived from 500°C calcination temperature at different milling duration as well as sintering temperature

Figure 2 showed the correlation among dielectric value, milling duration (20, 40 and 60 mins) and sintering temperature. No significant evidence shown that longer milling time will enhance the dielectric constant performance. However, as for the sintering temperature, the is a significant increase of dielectric constant value by increasing the sintering temperature.

To further support the statement, we have increased the sintering temperature to 1450°C. It shown in figure 3 that higher dielectric constant is achieved as the sintering temperature increased to 1450°C. This phenomenon can be explained by the microstructure of the sintered pellets which is discussed later in this report. Samples which sintered at 1450°C consistently showing better dielectric constant performance.

Further increased of the sintering temperature is not attempted as higher sintering temperature will induced phase changes in BST for liquidified sintering.

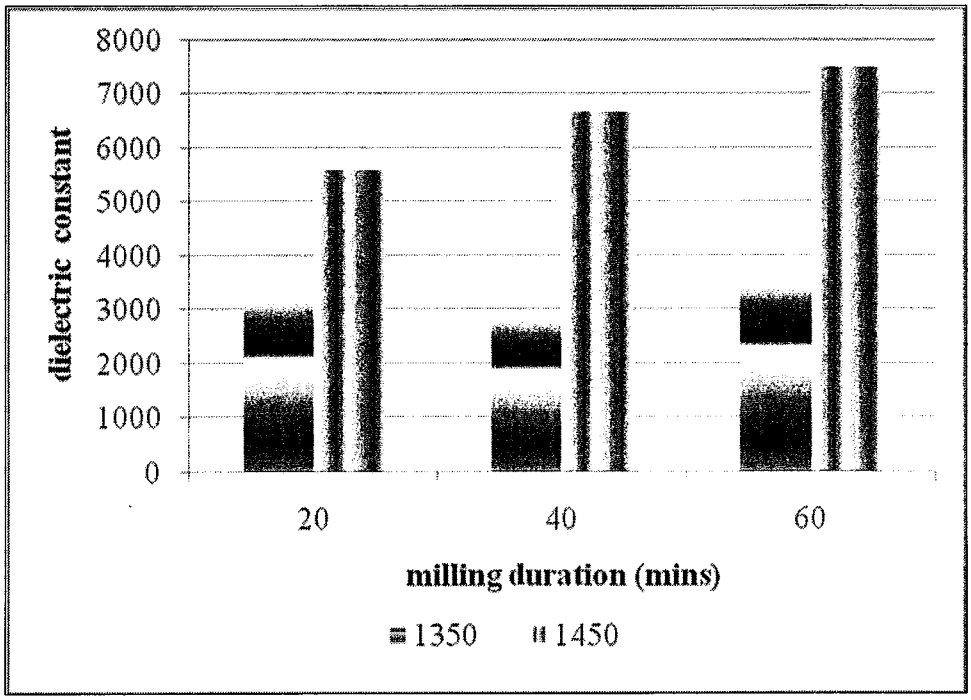


Figure 3: Dielectric constant composrison between samples sintered at 1350°C and 1450°C

The phase analysis of sintered pellets

XRD phase analysis was performed to investigate any phase changes occurred at 1450°C sintering which might lead to increased of the dielectric constant value. Figure 4 showed the XRD pattern of both samples which sintered at 1250°C and 1450°C, both diffractogram are similar indicating the presence of single phase BST. Hence, the increased of dielectric value was not phase-change related. It is also proven that BST phase are stable in the range of sinteing temperature of 1250°C to 1450°C.

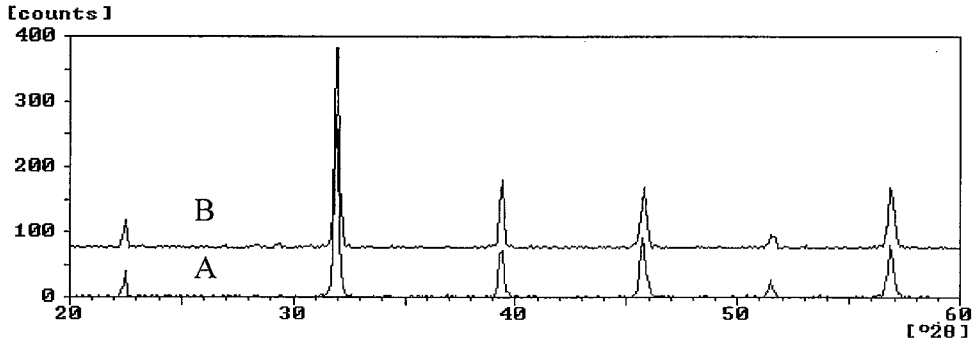
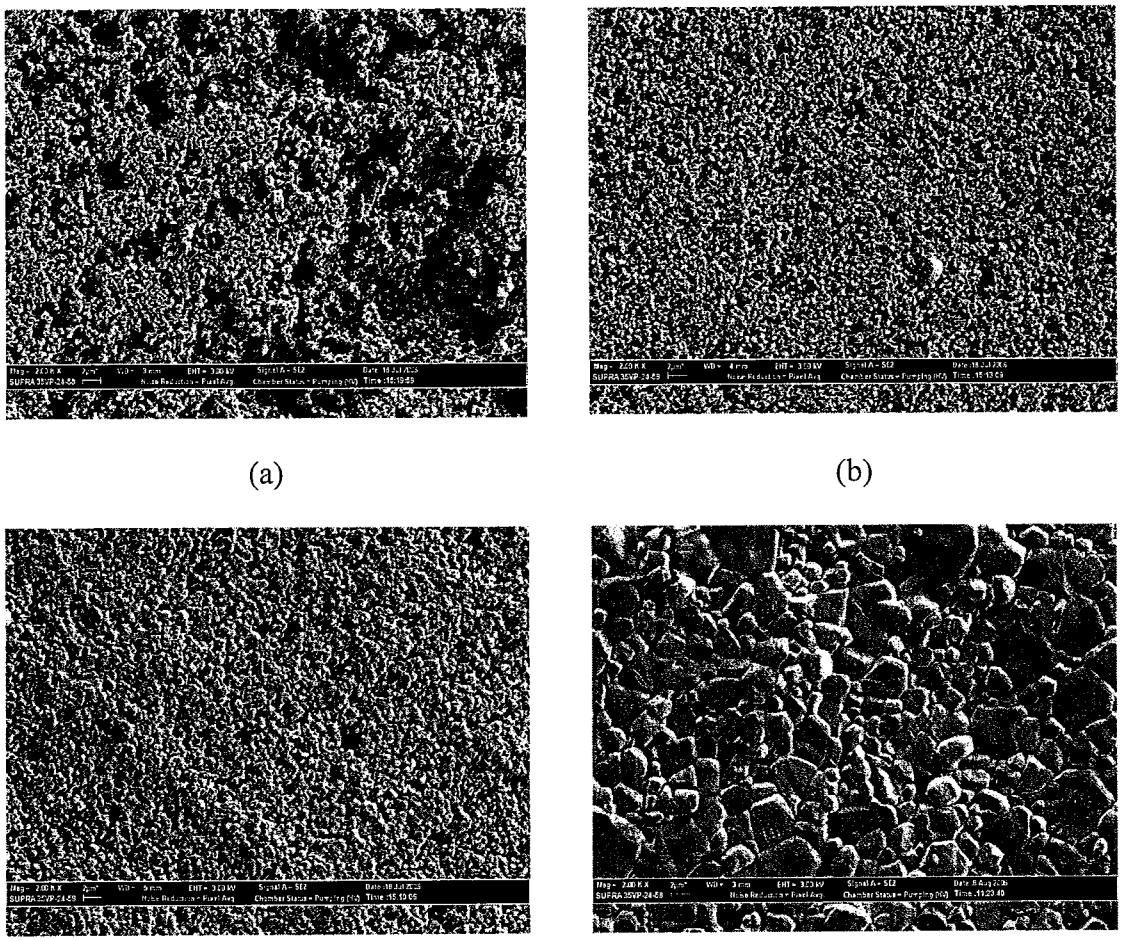


Figure 4: XRD for sample (A) sintered at 1250°C and (B) sintered at 1450°C

The microstructure of the sintered pellets

The microstructure of the sintered pellet had been investigated. Figure 5 showed the microstructure of the sintered pellet at different temperature. Significant different of microsctructure was observed, at 1250°C the pellet is extremely porous. For sample sintered at 1300°C and 1350°C, relatively it is less porous however the particles are still not sintered properly. For sample sintered at 1450°C, a dense microstructure was observed with the grain size in the average of 1 μm. These significant changes of microstructure against the sintering time explained the dielectric value difference shown in figure 2 and 3. A fully dense pellet will enhanced the dielectric properties. However, that is not the only factor that influenced the dielectric properties; other parameters such as purity, sintered grain size, uniformity of the grain size etc. play a role in determining the dielectric properties as well.

Pellet sintered at 1450°C shown in figure 5 (d) possessed wide range of grain size, this was due to the nature of planetary milling mechanism which commonly induced caking effect to the solid system, hence certain solid was intensively milled (espeacilly those have higher surface contact with milling media).



(a) (b)

(c) (d)

Figure 5 Microstructure of BST pellet samples sintered at (a) 1250°C, (b) 1300°C, (c) 1350°C and (d) 1450°C

The TEM morphology and phase analysis of calcined powder

Figure 6: TEM powder morphology of the calcined powder

Figure 6 showed the particle morphology of the calcined powder. Ultrafine particle size are ranging from 100 to 300nm. However, most of the particles are highly agglomerated after the mechanical activation process due to the high energy impact from the milling media. The elongated particles are believed to be $BaCO_3$ and $SrCO_3$ based on our previous research on $BaCO_3$-$SrCO_3$-TiO_2 solid system studies. Phase analysis in figure 7 showed that dominant phase of BST was found, however there are remnant of carbonates phase in the mixture. This is in agreement with the TEM result which shown formation $BaCO_3$ as well as $SrCO_3$ in the calcined mixture. Formation of carbonates took place when the BaO and SrO (which is the resultant of decomposition of $Ba(OH)_2.8H_2O$ and $Sr(OH)_2.8H_2O$) reacted with CO_2 in air instead of TiO_2, indirectly indicating that the solid mixture was not able to homogenously mixed.

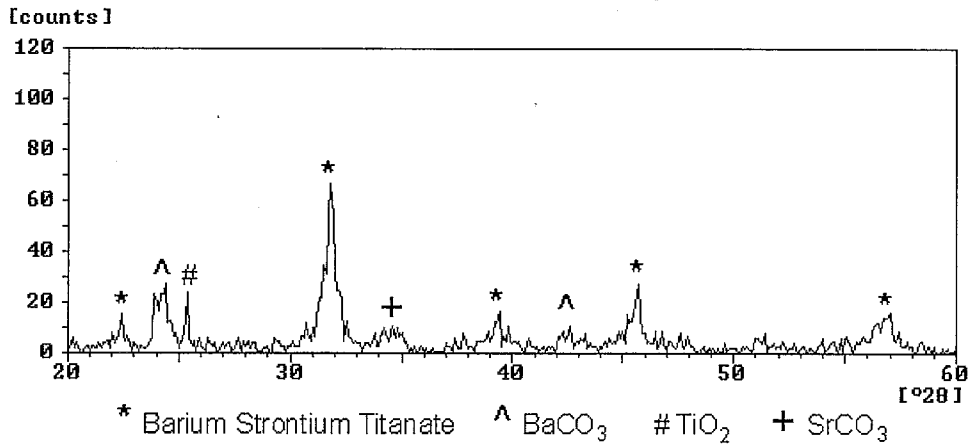


Figure 7: XRD diffractogram of calcined $Ba(OH)_2.8H_2O$-$Sr(OH)_2.8H_2O$-TiO_2 mixture

Overall Discussion

In this studies, we had produced single phase BST pellet by applying calcination temperature as low as 500°C. The major challenge in applying mechanical activation technique to the solid system was to overcame the caking problem.

The planetary milling mechanism is shown in figure 8, the powder is primarily crushed by the high energy impact of grinding balls together with friction between the balls and the wall of the grinding bowl. The grinding balls and the powder in the grinding bowl are acted upon by the centrifugal forces due to the rotation of the grinding bowl about its own axis and due to the rotating supporting disc. The grinding bowl and the supporting disc rotate in opposite directions, so that the centrifugal forces alternately act in the same and opposite directions. This results in, as a frictional effect, the grinding balls running along the inner wall of the bowl, and as an impact effect, the balls impacting against the opposite wall of the grinding bowl. The impact effect is enhanced by the grinding balls impacting against one another.

However, one of the drawbacks in this system is that the powder in the milling jar adhered to the milling jar as well as the milling balls; this phenomenon is referred as caking. The caking problem increased when higher speed was applied in the planetary milling resulting in hard caking which are difficult to scrap off from the milling jar. Caking problem caused immobility of the particles and thus restrained the mixing process.

Figure 9 showed the photo of the mixture which is planetary milled. After planetary milling minimum loose powder are found the bowl, majority of the solids are "caked" to the wall of the jar.

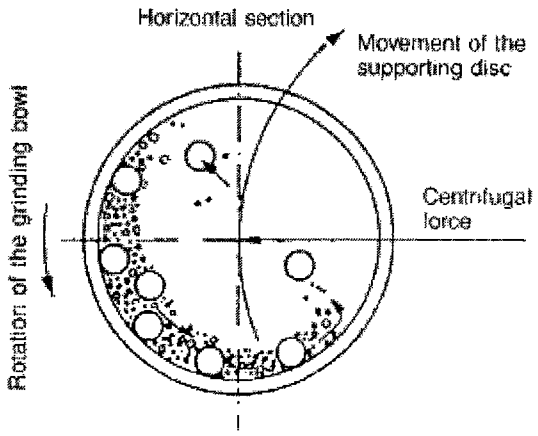


Figure 8: Schematic planetary milling mechanism

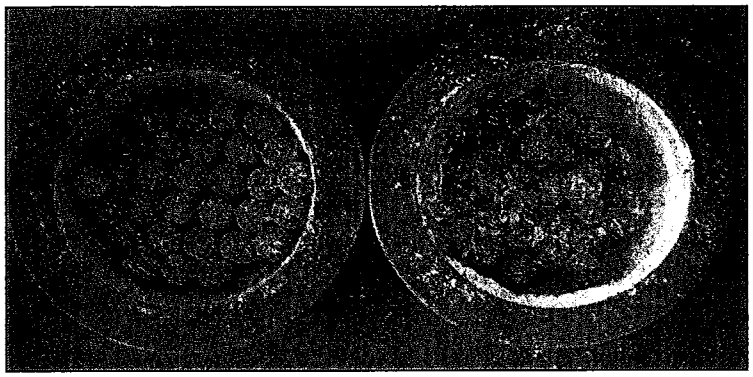
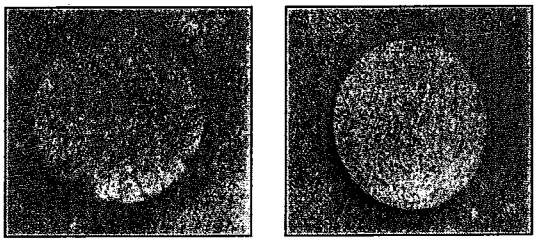


Figure 9: Powder caking after planetary milling

Calcination at 500°C is the lowest that we can achieved in this study. Figure 10 showed the comparison of the sintered pellets prepared from 400°C and 500°C calcined mixture. The pellets prepared from 400°C calcined mixture cracked after sintering, this is due to insufficient decomposition at 400°C. Further significant decompostion took place during sintering which caused the pellet to crack.



(a) (b)

Figure 10: Sintered pellets derived from mixture calcined at (a) 400°C and (b) 500°C

The dielectric properties obtained in this studies are relatively low as compared to those derived from conventional solid state reaction route. The dielectric properties are most optimum in the grain size range of 2-5 μm, and subsequent declined if the grain size

is smaller or bigger. Therefore ultrafine powder is expected to yield lower dielectric value, however it makes miniaturization possible which is crucial in electronic field.

Figure 11 showed the grain size of 1300°C sintered pellets, it has a porous structure with the grain size at the low end of submicron. Ultrafine particles derived from mechanical activation prone to form agglomeration due to their large surface area as well as the caking effect. The agglomerates transformed into aggregates during calcination process and therefore resulting in greater variance of the particle distribution, it minimized the numbers of contact points among the particles thus resulting in poorer sinterability. Furthermore, the decomposition of the remnant phase of $BaCO_3$ and $SrCO_3$ in the calcined powder contributed to the porous microstructure; hence degraded the dielectric properties.

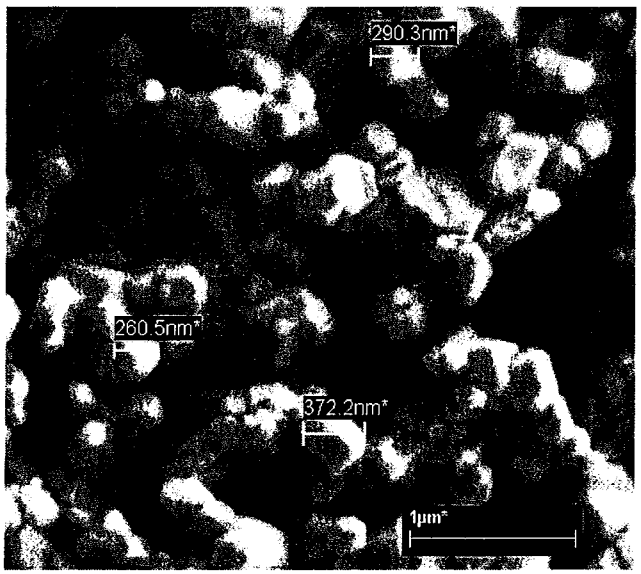


Figure 11: Microstructure of pellet sintered at 1300°C